

NASA CONTRACTOR
REPORT

NASA CR-30

18p



NASA CR-30

N64-15968

CODE-1

double code
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N64-15968

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PRESENCE OF MERCURY AND CESIUM

by William Rostoker (IIT Res. Inst) Mar. 1964 18p ref

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(NASA)

Prepared under Contract No. NAS 3-2251 by

IIT RESEARCH INSTITUTE

Chicago, Illinois

for

(NASA CR-30; ARF-B3501-B41) OFBI \$0.50

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ARF R3501-B41, September 4, 1962.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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DETERIORATION OF SOME ALUMINUM ALLOYS IN THE PRESENCE OF MERCURY AND CESIUM¹

By William Rostoker

I. INTRODUCTION

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Existing plans for the space propulsion environmental facility (NASA Lewis Research Center) call for the use of weldable, high-strength aluminum alloy in the inner chamber construction. This chamber will operate in high vacuum and at temperatures approaching liquid air. Within the chamber various space propulsion devices will be tested. It is expected that in spite of all reasonable precautions, some of the liquid metals in use will escape into the chamber and be deposited on the walls.

It is known that mercury and cesium under appropriate conditions, when in the liquid state wetted to aluminum alloys and in the presence of internal or external stresses, can lead to brittle rupture of the aluminum. It is also known that certain abnormal corrosion effects are to be expected when liquid mercury or cesium is in contact with aluminum in the presence of moist air. The embrittlement effects occur only when the mercury or cesium is molten. This is also the case with mercury corrosion. Cesium corrosion, however, as will be explained later, can occur at initial temperatures below the melting point. These remarks are intended to point to the fact that the deposits on the chamber walls during operation at low temperatures are themselves not likely to constitute a hazard. However, after shutdown, warming up, and breaking the vacuum a potentially hazardous condition exists. The magnitude of the hazard is the objective of the work herein reported.

Author

II. THE NATURE OF EMBRITTLEMENT BY LIQUID METALS

It is useful as a basis for the presentation of this work to give a brief résumé of the phenomenon of embrittlement by liquid metals. Many liquid metals on prolonged exposure to a higher melting point metal will diffuse into the body of the latter producing brittle coatings which impair the ductility of the whole load-supporting section. Such is the case of copper immersed in molten tin. Certain liquid metals will penetrate a

¹Additional information is presented in "Embrittlement of Liquid Metals" by William Rostoker, J. M. McCaughey, and H. Markus. Reinhold Publishing Corp., 1960.

polycrystalline solid metal along intercrystalline paths given sufficient time , at a proper temperature . Envelopment of aluminum crystals or grains by molten gallium is a case in point.

These two embrittlement processes are easily observed and easily understood. A third and much more catastrophic embrittlement can occur whose nature and origin are not at all obvious. A solid metal is in jeopardy by the simple act of wetting with certain low melting point metals. Cracking initiates at that interface and propagates in a general direction transverse to the axis or axes of principal tensile stresses. The conjoint existence of a liquid-solid interface and a critical magnitude of tensile stress is the necessary condition for the occurrence of fracture. The stress may be continuously increasing as in the simple tensile test, static, or alternating. The stresses may be externally applied or residual from prior mechanical or thermal history.

We will at this point list some of the characteristics of this form of liquid metal embrittlement:

(a) Not every liquid metal will embrittle every structural metal even with the establishment of a true wetted interface. In the case of aluminum alloys, the effective ones are liquid Hg, Ga, alkali metals, In, and Sn. Molten Pb, Bi, Cd, and Li are not effective.

(b) Neither the area wetted nor the amount of liquid present need be very large although the amount of the latter limits the extent of cracking.

(c) Fractures in recrystallized metals are invariably intercrystalline except in the case of elongated grain structures. However, transcrystalline fracture can be produced in heavily cold-worked metals and in certain single crystals.

(d) Embrittlement can be encountered in all degrees from slight reduction in total ductility to brittle fracture well below the engineering yield point. In the case of Al 1100-O wetted with Hg, only some loss in tensile ductility is encountered but Al 2024-T4 can be made to fail at 20% of its yield stress.

(e) Brittle fracture is potential at the moment of wetting if the stress is high enough; but if the stress is lower, a finite delay time is associated with fracture which is proportionate to the stress level. We may therefore conceive of a static fatigue relationship.

(f) In a general way the fracture stress in the wetted condition is dependent on the hardness of the metal. The harder alloys are more prone to embrittlement. Age-hardened alloys are more prone to embrittlement than simple solid solution alloys hardened by cold working.

Of the two metals, Hg and Cs, prior experience indicates that molten Hg has the greater embrittling effect. Moreover, Cs reacts with air quickly to revert to an oxide or hydroxide form.

It must be emphasized that Hg is a hazard only when it wets Al. This is not easy to achieve. Acid halide or alkali hydroxides are usually required to induce wetting. Mercuric chloride is also an effective wetting agent in addition to plating out metallic mercury. A wetted condition of Hg on Al is transient. There is a strong tendency in the presence of air for de-wetting to occur, often in minutes, but sometimes in a matter of hours. Cesium, on the other hand, by forming hygroscopic hydroxides can wet Al without assistance.

III. CORROSION OF ALUMINUM ALLOYS BY MERCURY AND CESIUM

The processes of corrosion of Al alloys by Hg and Cs are quite different. Cs by reaction with moist air reacts to form hygroscopic hydroxides in which Al is soluble. However, the extent of attack is proportionate simply to the amount of Cs present per unit area of Al surface.

The action of Hg wetted to Al is more subtle. Al dissolves into molten Hg to a minor extent and Hg is easily saturated. But Al atoms in Hg solution at the Hg-air surface react and literally combust to form the oxide or hydrated oxide. By depleting the Al in Hg, more must be dissolved from the underlying massive Al and this process goes on and on converting Al to oxide until the mercury de-wets from the Al. In principle, if de-wetting did not occur, a small drop of Hg could bore a hole through a thick plate of Al.

IV. SCOPE OF WORK

The short evaluation program to be described was intended to supplement existing information. It is known, for example, that the 1100-O alloy wetted with mercury fails ductilely with only a minor loss of total ductility in uniaxial tension. But the intended application will involve biaxial stresses, and there are no existing data to indicate whether this stress condition influences the fracture behavior. There are no data on the delayed failure characteristics of either the 1100-O or 5083-O alloys wetted with mercury. In the event that the 5083-O alloy is unsuitable, the question remains whether the more dilute Mg contents in the 5052-O and 5454-O alloys might be more suitable. Finally, there are only general observations on the corrosion behavior of Al alloys in the presence of Hg and Cs. Although not specifically planned at the outset, interest by NASA in the possible use of Al plate clad with austenitic stainless steel was aroused recently. To satisfy preliminary questions some elementary tensile tests were made of stainless steel wetted with either Hg or Li.

The following is a summary of the several tasks undertaken:

- (a) Testing the 1100-O alloy wetted with Hg to failure in biaxial tension.
- (b) Measurement of the time to failure under static loading of the 1100-O and 5083-O alloys wetted with Hg at stress levels below the tensile fracture limit and for times up to one month.
- (c) Measurement of the uniaxial tensile fracture limits of the 5052-O and 5454-O alloys wetted with Hg.
- (d) Measurement of the corrosion rate of 1100-O and 5083-O alloys wetted with Hg for times up to one week.
- (e) Measurement of the corrosion rate as in (d) but wetted with Cs.
- (f) Measurement of the uniaxial tensile fracture limits of AISI 321 stainless steel wetted with molten Hg or Li.

All specimens were provided ready for testing by the Kaiser Aluminum Company (Spokane). Machined specimens were heat treated after machining in their preparation.

V. EXPERIMENTAL TECHNIQUES

The most difficult part of studying the deterioration of Al alloys in the presence of Hg is the establishment and maintenance of wetting of the Al by molten Hg. By whatever technique used, a solid specimen of Al superficially wetted with Hg will attempt to de-wet. Actual wetting may exist for less than 10 minutes or last for several hours. In a few instances, it has been possible to maintain obvious wetting for some days. Reliable techniques to prolong wetting for more than an hour do not exist. The attitude taken in this work was to make every effort to prolong wetting consistent with trying to achieve conditions of maximum hazard.

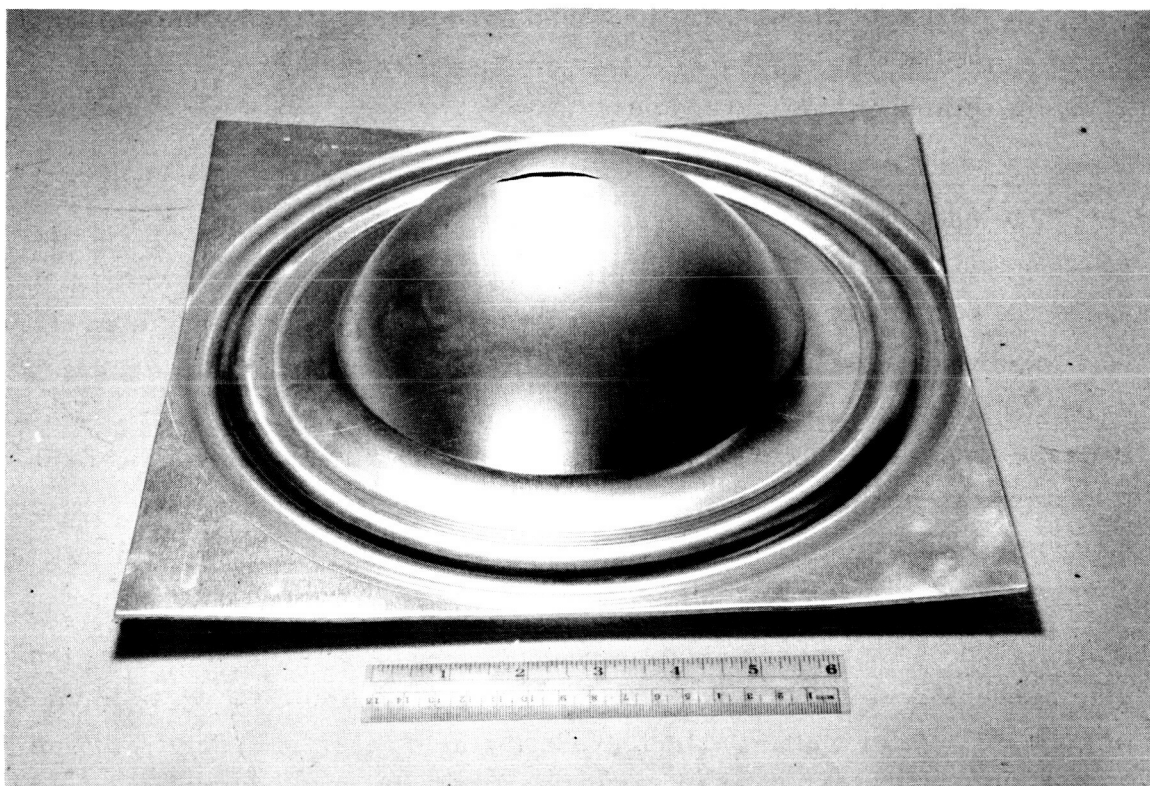
Two techniques seem most suitable. One involves etching the aluminum oxide with HF and wetting with metallic liquid Hg while immersed in the acid. After wetting is achieved, the acid must be nearly removed to reduce the corrosive attack over long periods. For short-time tests, the acid is best kept on the sample. Its presence does not of itself induce any embrittlement.

The other technique involves the use of a saturated aqueous solution of HgCl_2 . The solution itself dissolves aluminum oxide and plates out metallic liquid mercury by chemical displacement. In general, wetting by HgCl_2 solution resists de-wetting longer.

The biaxial stress tensile limit of Al alloy sheet was determined by the use of a hydraulic bulge testing device which clamps a disk of the metal of about 12 inches diameter. At the crown of the bulge the stress is in balanced biaxial tension. The ductility of the specimen was determined by increased spacing of gauge marks on the initial surface of the sheet and by reduction in thickness at failure. Actual ruptured specimens are illustrated in Figures 1 and 2.

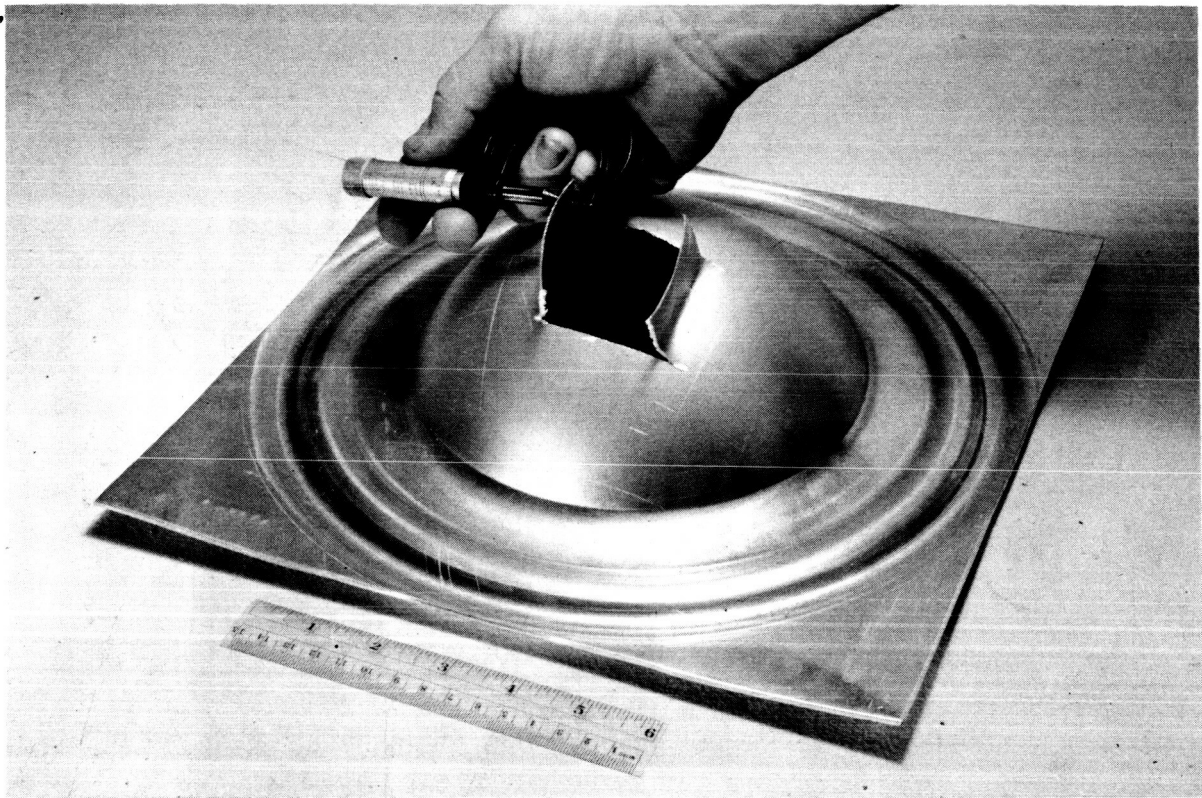
The manner of delayed failure testing is illustrated in Figure 3. A small Lucite capsule with a semicircular cavity was taped to the tensile specimen. To achieve wetting, the capsule on the specimen under load was

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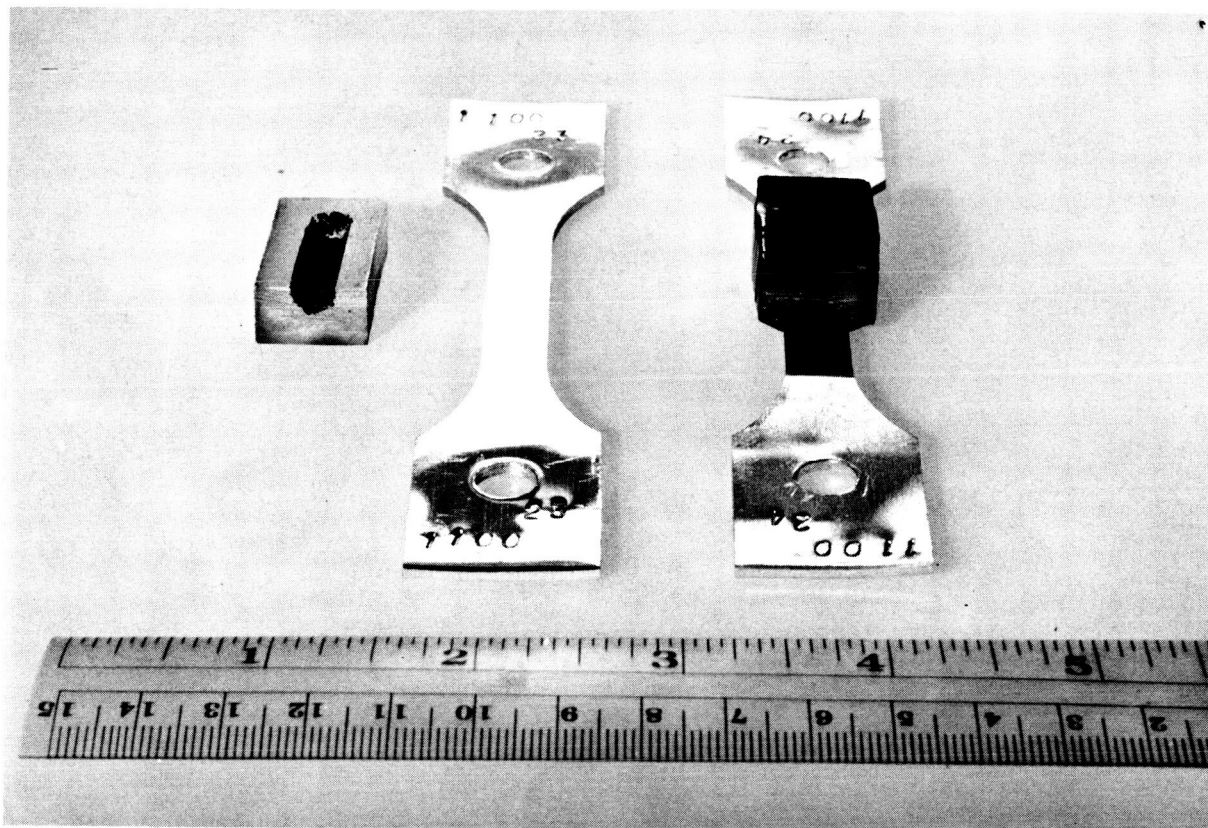
Neg. No. 23292

FIG. 1 - PHOTOGRAPH OF RUPTURED BULGE SPECIMEN
(1100-O ALLOY) Initial blank size: 12 in. x 12 in.
x 0.090 in.



Neg. No. 23293

FIG. 2 - PHOTOGRAPH OF RUPTURED BULGE SPECIMEN
CUT OPEN AFTER FAILURE FOR MEASURING
THICKNESS REDUCTION.



Neg. No. 23291

FIG. 3 - PHOTOGRAPH OF DELAYED FAILURE
TENSILE SPECIMEN, LUCITE CAPSULE,
AND ASSEMBLY.

Tensile specimen: 5 1/2 in. long, 0.375 in. x 1 1/2 in.
test section, 0.065 in. thick. Heat-treated to "O" con-
dition after machining. Original rolled surfaces undis-
turbed.

filled with the HgCl_2 solution which on wetting plated Hg out on the test length of the specimen. The remaining solution was then displaced with metallic mercury so that during the period of the test, the capsule cavity was filled with Hg. From time to time during the test period, a few drops of HgCl_2 solution were added to the top of the Hg pool to re-establish wetting if necessary. Under these conditions it was not possible to observe whether de-wetting had occurred. Stressing was maintained by conventional lever arm creep machines.

Tensile testing was performed by the use of a micro-tensile machine called a Tensometer. This machine permits plotting of a stress-strain curve, and the determination of a yield stress which corresponds to about 0.2% strain. The tensile properties of conventional metals replicate well on this machine those yield and ultimate strengths given by larger and more common machines. The yield strength data given in a later section demonstrate this.

Corrosion testing was performed under an atmosphere of hot moist air which by previous experience appears to maximize the rate of the process. This was accomplished as follows: The wetted specimens (1 in. x 1 in. x 1/4 in. thick) were placed inside a heavily insulated glass tube. At one end air was introduced, which had been bubbled through a water bath maintained at a suitable temperature by thermostatic control. The rate of moisture-soaked air passage was regulated so that a thermometer immediately above the specimen registered a steady 50°C . Only one specimen occupied each tubular chamber. The glass tube was corked at the exit end and tilted slightly to permit drainage of water condensate as it formed.

VI. EXPERIMENTAL RESULTS

A. Failure of 1100-O Alloy in Biaxial Tension

In uniaxial tension and unwetted, the 1100-O alloy gives about 42% elongation at failure. When wetted with mercury, the elongation is reduced to 23-33%. In bulge testing at the crown of the bulge, the plates gave an average of 63% reduction in thickness and 50% elongation on 2 1/2 inches when unwetted. Wetting with mercury gave 69% reduction in thickness and 48% average elongation at failure. With these results we may

conclude that mercury has no serious influence on the ductility of the 1100-O alloy. Since it is general experience that wetting with a liquid metal has no influence on the yield point, we can also say that the 1100-O alloy is also safe from a strength viewpoint. This point was actually confirmed in one set of uniaxial tension tests where yield points of 5500 psi (dry) and 4800 psi (wet), and tensile strengths of 12,850 psi (dry) and 12,710 psi (wet) were registered.

B. Uniaxial Tensile Properties of Aluminum-Magnesium

With the first set of specimens received from the Kaiser Aluminum Company (Spokane) the resulting tensile properties are summarized in Table I. It was apparent immediately that the 5083-O alloy was breaking at a significantly lower stress than experienced in previous work. It was also apparent that this material showed a large yield point elongation whereas previous material acquired in the Chicago area had shown little or none of this effect. The yield point elongation and slightly higher yield strength suggested a grain size difference. This was confirmed by the laboratories in Spokane, and a new set of specimens was sent out. This new set contained both fine- and coarse-grained specimens for comparison. The coarse-grained material was taken from thicker plate. The fine-grained material was finished rolled to final gauge. Comparative tensile behavior in the wetted and unwetted conditions are given in Table II, where it can be seen that the coarse-grained material failed in the presence of Hg at the yield point as in the case of the more dilute alloys 5052 and 5454.

In consideration of these three alloys and their propensity for embrittlement in the presence of Hg, there seems no reason to choose the softer alloys. In terms of unwetted yield strength and wetted fracture strength, the 5083-O alloy is superior provided that proper grain size control is maintained. The actual grain size limits will have to be determined more closely, but an appreciation of this can be gained from the microstructures illustrated in Figure 4.

C. Delayed Failure of 1100-O and 5083-O Alloys Wetted with Mercury

The 1100-O alloy wetted with Hg as described earlier was loaded to 80, 90% respectively of the engineering yield stress, and specimens were

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TABLE I

TENSILE PROPERTIES OF ALUMINUM ALLOYS

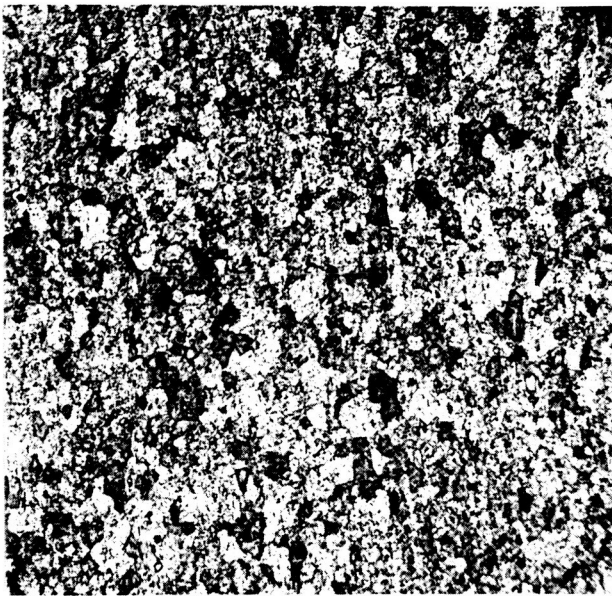
5052-O, 5454-O, AND 5083-O

Alloy	Condition	Yield Stress, psi	Fracture Stress or UTS, psi	Elongation, %
5052-O	Dry	11,780	29,400	19
	Wetted with Hg		12,600	0-4
5454-O	Dry	14,450	36,400	17
	Wetted with Hg		14,800	0-2
5083-O	Dry	22,100	44,300	24
	Wetted with Hg		13,300	0

TABLE II

COMPARATIVE TENSILE BEHAVIOR
OF FINE- AND COARSE-GRAINED 5083-O ALLOY

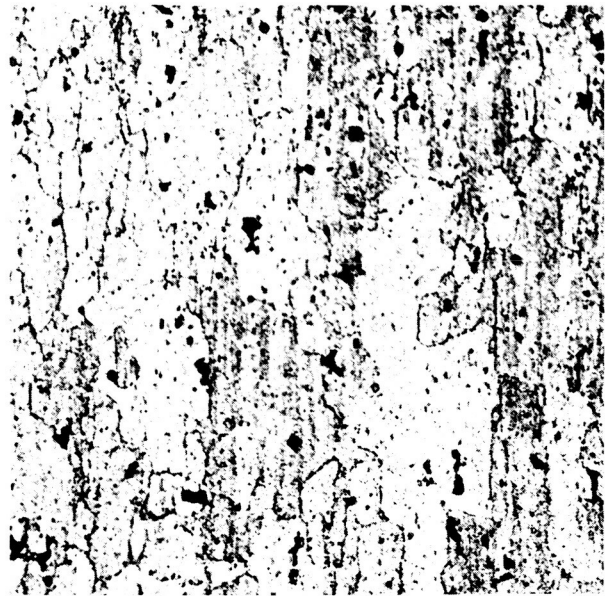
Material	Condition	Yield Stress, psi	Fracture Stress or UTS, psi	Elongation, %
Fine grain	Dry	22,500	46,300	23
	Wetted with Hg		10,250	0
Coarse grain	Dry	18,650	46,100	20
	Wetted with Hg		18,250	0



Neg. No. 23473

X250

(a) Fine-grain condition, as finish-rolled strip.



Neg. No. 23472

X250

(b) Coarse-grain condition, as machined from thicker plate.

FIG. 4 - COMPARISON OF THE MICROSTRUCTURES OF 5083-O ALLOY IN FINE AND COARSE GRAIN CONDITIONS (Etched in 30% H_3PO_4).

- maintained at those loads for 31 days without indication of failure.

The original fine-grain 5083-O withstood a stress of only 36% of the engineering yield stress for 32 days but failed in 87 minutes at 42% of the yield stress. The coarse-grain material withstood 90% of the yield stress for 30 days without failure.

This reinforces the obvious conclusion that for maximum security from embrittlement by Hg, the grain size of the 5083 alloy must be controlled.

D. Tensile Properties of 321 Stainless Steel
Wetted with Mercury or Lithium

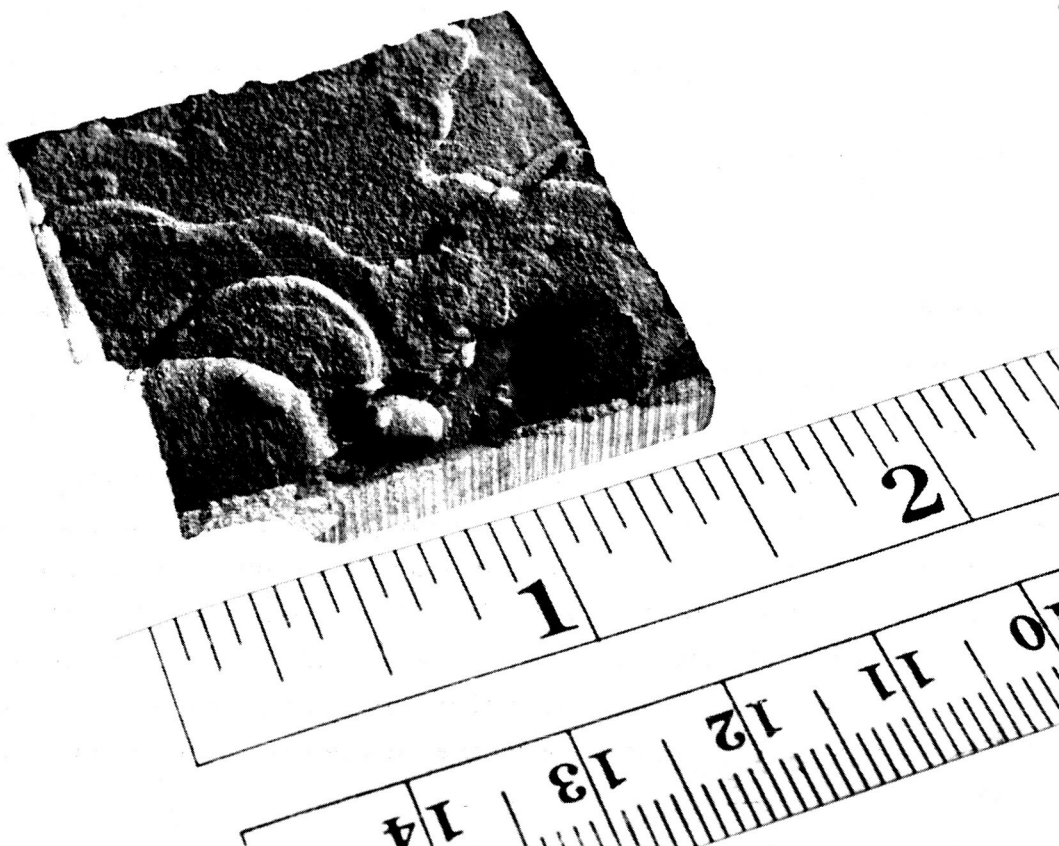
AISI 321 grade is a weldable austenitic stainless steel of the type that should be used for cladding to Al alloy plate. It was found possible to coat this alloy with Hg by reacting for a long time in a concentrated solution of HgCl_2 . In order to work with molten Li it is necessary to test at 200°C , at which temperature molten Li will remove oxide films and autogenously wet to stainless steel. It was found that Hg at room temperature and Li at 200°C had absolutely no influence on the tensile properties of the stainless steel.

E. Corrosion of 1100-O and 5083-O Alloys
in the Presence of Mercury

These tests gave very erratic results depending on the time for de-wetting. It was never possible to sustain the wetted condition on 1100-O for very long, but on two occasions wetting persisted on the 5083 alloy for several days with consequently serious corrosion. One of these specimens is illustrated in Figure 5.

The results of loss in cross section are summarized in Table III. It must be remarked at this point that the corroded surfaces were very rough and covered with a porous white film which is likely to be highly absorptive of water.

In general, the 1100-O alloy seems quite resistant to this form of corrosive attack even under maximum conditions of hazard.



Neg. No. 23399

X2

FIG. 5 - PHOTOGRAPH SHOWING CORROSION OF
5083-O ALLOY.

Coupon (1 in. x 1 in. x 1/4 in.) had been wetted with Hg and exposed to 50°C, water-saturated air flow for 4 days. This is an unusually exaggerated example of corrosion.

TABLE III

CORROSION PENETRATION OF 1100-O AND 5083-O ALLOYS
WETTED WITH MERCURY AND MAINTAINED IN 50°C,
MOISTURE-SATURATED MOVING AIR

Material	Time of Exposure, hours	Loss in Cross*Section, inches
1100-O	18	0.016
	24	0.024
	53	0.002
	63	0.020
	72	0.019
	96	0.003
5083-O	15	0.016
	24	0.041
	53	0.028
	63	0.015
	72	0.086
	96	0.123

* Loss in cross section was not uniform. Data given are maximum penetrations. Initial thickness 0.250 in.

F. Corrosion of 1100-O and 5083-O Alloys
in the Presence of Cesium

Cesium reacting to form CsOH is hygroscopic and converts to a caustic solution. The resultant attack was only superficial. More attack was observed in normal room temperature air with ambient humidity than in the 50°C moisture-saturated moving air. This is because water condensate gradually washed away the caustic solution. In the latter case, penetrations did not exceed 0.007 in. in 5 days. In room ambient conditions, the penetration rose to 0.010 in. over a period of 14 days.

VII. SUMMARY

In general, it can be stated that neither Hg nor Cs is likely to present any hazard either from embrittlement or corrosion to a 5083-O plate clad generously with 1100-O on those surfaces exposed to the designated liquid metals. For maximum protection, the 5083-O alloy should be in a coarse-grained condition.

A cladding with austenitic stainless steel will preclude both embrittlement and any corrosive attack.